7-17-80

METHOD 11—DETERMINATION OF HYDROGEN SULFIDE EMISSIONS FROM STATIONARY SOURCES [5]

1. *Principle and applicability.*

1.1 *Principle.* Hydrogen sulfide (H_2S) is collected from the source in a series of midget impingers and reacted with alkaline cadmium hydroxide [$Cd(OH)_2$] to form cadmium sulfide (CdS). The precipitated CdS is then dissolved in hydrochloric acid and absorbed in a known volume of iodine solution. The iodine consumed is a measure of the H_2S content of the gas. An impinger containing hydrogen peroxide is included to remove SO_2 as an interfering species.

1.2 *Applicability.* This method is applicable for the determination of hydrogen sulfide emissions from stationary sources only when specified by the test procedures for determining compliance with the new source performance standards.

2. *Apparatus.*

2.1 *Sampling train.*

2.1.1 *Sampling line*—6- to 7-mm (¼-inch) Teflon [1] tubing to connect sampling train to sampling valve, with provisions for heating to prevent condensation. A pressure reducing valve prior to the Teflon sampling line may be required depending on sampling stream pressure.

2.1.2 *Impingers*—Five midget impingers, each with 30-ml capacity, or equivalent.

2.1.3 *Ice bath container*—To maintain absorbing solution at a constant temperature.

2.1.4 *Silica gel drying tube*—To protect pump and dry gas meter.

2.1.5 *Needle valve, or equivalent*—Stainless steel or other corrosion resistant material, to adjust gas flow rate.

2.1.6 *Pump*—Leak free, diaphragm type, or equivalent, to transport gas. (Not required if sampling stream under positive pressure.)

2.1.7 *Dry gas meter*—Sufficiently accurate to measure sample volume to within 1 percent.

2.1.8 *Rate meter*—Rotameter, or equivalent, to measure a flow rate of 0 to 3 liters per minute (0.1 ft^3/min).

2.1.9 *Graduated cylinder*—25 ml.

2.1.10 *Barometer*—To measure atmospheric pressure within ±2.5 mm (0.1 in.) Hg.

2.2 *Sample Recovery.*

2.2.1 *Sample container*—500-ml glass-stoppered iodine flask.

2.2.2 *Pipette*—50-ml volumetric type.

2.2.3 *Beakers*—250 ml.

2.2.4 *Wash bottle*—Glass.

2.3 *Analysis.*

2.3.1 *Flask*—500-ml glass-stoppered iodine flask.

2.3.2 *Burette*—One 50 ml.

2.3.2 *Flask*—125-ml conical.

3. *Reagents.*

3.1 *Sampling.*

3.1.1 *Absorbing solution*—Cadmium hydroxide ($Cd(OH)_2$)—Mix 4.3 g cadmium sulfate hydrate ($3\ CdSO_4 \cdot 8H_2O$) and 0.3 g of sodium hydroxide (NaOH) in 1 liter of distilled water (H_2O). Mix well.

Note: The cadmium hydroxide formed in this mixture will precipitate as a white suspension. Therefore, this solution must be thoroughly mixed before using to ensure an even distribution of the cadmium hydroxide.

3.1.2 *Hydrogen peroxide, 3 percent*—Dilute 30 percent hydrogen peroxide to 3 percent as needed. Prepare fresh daily.

3.2 *Sample recovery.*

3.2.1 *Hydrochloric acid solution (HCl), 10 percent by weight*—Mix 230 ml of concentrated HCl (specific gravity 1.19) and 770 ml of distilled H_2O.

3.2.2 *Iodine solution, 0.1 N*—Dissolve 24 g potassium iodide (KI) in 30 ml of distilled H_2O in a 1 liter graduated cylinder. Weigh 12.7 g of resublimed iodine (I_2) into a weighing bottle and add to the potassium iodide solution. Shake the mixture until the iodine is completely dissolved. Slowly dilute the solution to 1 liter with distilled H_2O, with swirling. Filter the solution, if cloudy, and store in a brown glass-stoppered bottle.

3.2.3 *Standard iodine solution, 0.01 N*—Dilute 100 ml of the 0.1 *N* iodine solution in a volumetric flask to 1 liter with distilled water.

Standardize daily as follows: Pipette 25 ml of the 0.01 *N* iodine solution into a 125-ml conical flask. Titrate with standard 0.01 *N* thiosulfate solution (see paragraph 3.3.2) until the solution is a light yellow. Add a few drops of the starch solution and continue titrating until the blue color just disappears. From the results of this titration, calculate the exact normality of the iodine solution (see paragraph 5.1).

3.2.4 *Distilled, deionized water.*

3.3 *Analysis.*

3.3.1 *Sodium thiosulfate solution, standard 0.1 N*—For each liter of solution, dissolve 24.8 g of sodium thiosulfate ($Na_2S_2O_3 \cdot 5H_2O$) in distilled water and add 0.01 g of anhydrous sodium carbonate (Na_2CO_3) and 0.4 ml of chloroform ($CHCl_3$) to stabilize. Mix thoroughly by shaking or by aerating with nitrogen for approximately 15 minutes, and store in a glass-stoppered glass bottle.

Standardize frequently as follows: Weigh into a 500-ml volumetric flask about 2 g of potassium dichromate ($K_2Cr_2O_7$) weighed to the nearest milligram and dilute to the 500-ml mark with distilled H_2O. Use dichromate which has been crystallized from distilled water and oven-dried at 182°C to 199°C (360°F to 390°F). Dissolve approximately 3 g of potassium iodide (KI) in 50 ml of distilled water in a glass-stoppered, 500-ml conical flask, then add 5 ml of 20-percent hydrochloric acid solution. Pipette 50 ml of the dichromate solution into this mixture. Gently swirl the solution once and allow it to stand in the dark for 5 minutes. Dilute the solution with 100 to 200 ml of distilled water, washing down the sides of the flask with part of the water. Swirl the solution slowly and titrate with the thiosulfate solution until the solution is light yellow. Add 4 ml of starch solution and continue with a slow titration with the thiosulfate until the bright blue color has disappeared and only the pale green color of the chromic ion remains. From this titration, calculate the exact normality of the sodium thiosulfate solution (see paragraph 5.2).[6]

3.3.2 *Sodium thiosulfate solution, standard 0.01 N*—Pipette 100 ml of the standard 0.1 *N* thiosulfate solution into a volumetric flask and dilute to one liter with distilled water.

3.3.3 *Starch indicator solution*—Suspend 10 g of soluble starch in 100 ml of distilled water and add 15 g of potassium hydroxide pellets. Stir until dissolved, dilute with 900 ml of distilled water, and let stand 1 hour. Neutralize the alkali with concentrated hydrochloric acid, using an indicator paper similar to Alkacid test ribbon, then add 2 ml of glacial acetic acid as a preservative.

Test for decomposition by titrating 4 ml of starch solution in 200 ml of distilled water with 0.01 *N* iodine solution. If more than 4 drops of the 0.01 *N* iodine solution are required to obtain the blue color, make up a fresh starch solution.

4. *Procedure.*

4.1 *Sampling.*

4.1.1 Assemble the sampling train as shown in Figure 11-1, connecting the five midget impingers in series. Place 15 ml of 3 percent hydrogen peroxide in the first impinger. Place 15 ml of the absorbing solution in each of the next three impingers, leaving the fifth dry. Place crushed ice around the impinger Add more ice during the run to keep th temperature of the gases leaving the las impinger at about 20°C (70°F), or less.

4.1.2 Purge the connecting line betwee the sampling valve and the first impinge Connect the sample line to the train. Recor the initial reading on the dry gas meter a shown in Table 11-1.

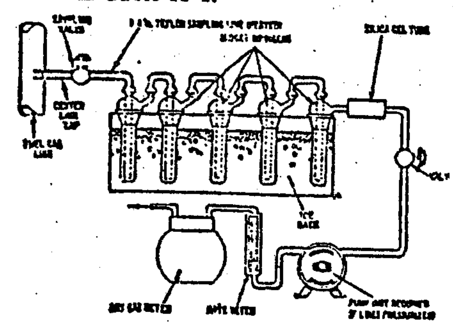

Figure 11-1. H_2S sampling train.

TABLE 11-1.—*Field data*

Location ____________ Comments:

Test ______________

Date ______________

Operator ___________

Barometric pressure___

Clock time	Gas volume through meter (V_m), liters (cubic feet)	Rotameter setting, Lpm (cubic feet per minute)	Meter temperature, °C (°F)

4.1.3 Open the flow control valve and ad just the sampling rate to 1.13 liters pe minute (0.04 cfm). Read the meter temper ature and record on Table 11-1.

4.1.4 Continue sampling a minimum of 1 minutes. If the yellow color of cadmium sul fide is visible in the third impinger, analyst should confirm that the applicable standar has been exceeded. At the end of the sampl time, close the flow control valve and rea the final meter volume and temperature.

4.1.5 Disconnect the impinger train from the sampling line. Purge the train with clea ambient air for 15 minutes to ensure that al H_2S is removed from the hydrogen peroxide Cap the open ends and move to the sampl clean-up area.

4.2 *Sample recovery.*

4.2.1 Pipette 50 ml of 0.01 *N* iodine solution into a 250-ml beaker. Add 50 ml of 10 percen HCl to the solution. Mix well.

4.2.2 Discard the contents of the hydrogen peroxide impinger. Carefully transfer the con tents of the remaining four impingers to 500-ml iodine flask.

4.2.3 Rinse the four absorbing impinger and connecting glassware with three portio of the acidified iodine solution. Use the en tire 100 ml of acidified iodine for this pur pose. Immediately after pouring the acidifie iodine into an impinger, stopper it and shak for a few moments before transferring th rinse to the iodine flask. Do not transfer an rinse portion from one impinger to another transfer it directly to the iodine flask. Onc acidified iodine solution has been poured int any glassware containing cadmium sulfid sample, the container must be tightly stop pered at all times except when adding mor solution, and this must be done as quickl and carefully as possible. After adding an acidified iodine solution to the iodine flask allow a few minutes for absorption of the H_2S into the iodine before adding any furthe rinses.

[1] Mention of trade names or specific products does not constitute endorsement by the Environmental Protection Agency.

4.2.4 Follow this rinse with two more rinses using distilled water. Add the distilled water rinses to the iodine flask. Stopper the flask and shake well. Allow about 30 minutes for absorption of the H_2S into the iodine, then complete the analysis titration.

Caution: Keep the iodine flask stoppered except when adding sample or titrant.

4.2.5 Prepare a blank in an iodine flask using 45 ml of the absorbing solution, 50 ml of 0.01 *N* iodine solution, and 50 ml of 10 percent HCl. Stopper the flask, shake well and analyze with the samples.

4.3 *Analysis.*

Note: This analysis titration should be conducted at the sampling location in order to prevent loss of iodine from the sample. Titration should never be made in direct sunlight.

4.3.1 Titrate the solution in the flask with 0.01 *N* sodium thiosulfate solution until the solution is light yellow. Add 4 ml of the starch indicator solution and continue titrating until the blue color just disappears.

4.3.2 Titrate the blanks in the same manner as the samples.

5. *Calculations.*

5.1 *Normality of the standard iodine solution.*

$$N_I=\frac{N_T V_T}{V_I} \qquad \text{equation 11-1}$$

where:

N_I=normality of iodine, g-eq/liter.
V_I=volume of iodine used, ml.
N_T=normality of sodium thiosulfate, g-eq/liter.
V_T=volume of sodium thiosulfate used, ml.

5.2 *Normality of the standard thiosulfate solution.*

$$N_T=2.04\frac{W}{V_T} \qquad \text{equation 11-2}$$

where:

W=weight of $K_2Cr_2O_7$ used, g.
V_T=volume of $Na_2S_2O_3$ used, ml.
N_T=normality of standard thiosulfate solution, g-eq/liter.
2.04=conversion factor

$$=\frac{(6\text{ eq }I_2/\text{mole }K_2Cr_2O_7)\ (1{,}000\text{ ml/l})}{(294.2\text{ g }K_2Cr_2O_7/\text{mole})\ (10\text{ aliquot factor})}.$$

5.3 *Dry gas volume.* Correct the sample volume measured by the dry gas meter to standard conditions [21°C(70°F)] and 760 mm (29.92 inches) Hg] by using equation 11-3.

$$V_{m_{std}}=V_m\left(\frac{T_{std}}{T_m}\right)\left(\frac{P_{bar}}{P_{std}}\right) \qquad \text{equation 11-3}$$

where:

$V_{m_{std}}$=volume at standard conditions of gas sample through the dry gas meter, standard liters (scf).
V_m=volume of gas sample through the dry gas meter (meter conditions), liters (cu. ft.).
T_{std}=absolute temperature at standard conditions, 294°K (530°R).
T_m=average dry gas meter temperature, °K (°R).
P_{bar}=barometric pressure at the orifice meter, mm Hg (in. Hg).
P_{std}=absolute pressure at standard conditions, 760 mm Hg (29.92 in. Hg).

5.4 *Concentration of H_2S.*—Calculate the concentration of H_2S in the gas stream at standard conditions using equation 11-4:

$$C_{H_2S}=\frac{K[(V_I N_I-V_T N_T)_{sample}-(V_I N_I-V_T N_T)_{blank}]}{V_{m_{std}}}$$

where (metric units):

C_{H_2S}=concentration of H_2S at standard conditions, mg/dscm
K=conversion factor=17.0×10^3

$$=\frac{(34.07\text{ g/mole }H_2S)(1{,}000\text{ l/m}^3)(1{,}000\text{ mg/g})}{(1{,}000\text{ ml/l})(2H_2S\text{ eq/mole})}$$

V_I=volume of standard iodine solution, ml.
N_I=normality of standard iodine solution, g-eq/liter.
V_T=volume of standard sodium thiosulfate solution, ml.
N_T=normality of standard sodium thiosulfate solution, g-eq/liter.
$V_{m_{std}}$=dry gas volume at standard conditions, liters.

where (English units):

$$K=0.263=\frac{17.0(15.43\text{ gr/g})}{(1{,}000\text{ l/m}^3)}$$

$V_{m_{std}}$=scf.
C_{H_2S}=gr/dscf.

6. *References.*

6.1 Determination of Hydrogen Sulfide, Ammoniacal Cadmium Chloride Method, API Method 772-54. In: Manual on Disposal of Refinery Wastes, Vol. V: Sampling and Analysis of Waste Gases and Particulate Matter, American Petroleum Institute, Washington, D.C., 1954.

6.2 Tentative Method for Determination of Hydrogen Sulfide and Mercaptan Sulfur in Natural Gas, Natural Gas Processors Association, Tulsa, Oklahoma, NGPA Publication No. 2265-65, 1965.